

METHOD AND APPARATUS FOR MAKING A CRYSTAL PRE-MELT

Background of Invention

[0001] The invention relates to methods and apparatus for making crystals. While not wishing to be bound to a particular group of crystals, it is convenient in the following discussion to focus on a particular group of crystals. One group of crystals of interest is optical fluoride crystals. Single-grained optical fluoride crystals are useful in applications requiring transmission at short wavelengths, e.g., in the vacuum ultraviolet region. At present, CaF_2 crystal is the most viable lens material for 157-nm microlithography.

[0002] Optical fluoride crystals as well as other types of crystals can be grown in two steps. The first step is a pre-melt step in which crystal raw material in powder or granular form is melted and then rapidly cooled into a solid body, which herein will be referred to as a crystal pre-melt. The second step is a growth step in which the crystal pre-melt is melted and then used to grow one or more crystals.

[0003] Single-grained crystals are commonly grown using the Bridgman-Stockbarger process. As illustrated in Figure 1A, the Bridgman-Stockbarger process takes place in a vertical furnace **100** having an upper zone **102** and a lower zone **104**. A middle or thermal gradient zone **106** is defined between the upper zone **102** and the lower zone **104** by making the temperature of the upper zone **102** higher than the temperature of the lower zone **104**. The growth step starts with loading of a crystal pre-melt **108** into a crystal growth crucible **110**. With the growth crucible **110** in the upper zone **102**, the upper zone **102** is then heated to a temperature sufficient to melt the crystal pre-melt **108**. After melting the crystal pre-melt **108**, the growth crucible **110** is lowered from the upper zone **102**, through the thermal gradient zone **106**, into the lower zone **104**. As shown in Figure 1B, as the growth crucible **110** passes through the thermal gradient zone **106**, a phase transition occurs inside the molten crystal pre-melt **108a**, creating a crystal front **112**. The crystal front **112** propagates inside the growth crucible **110**, within the molten crystal pre-melt **108a**, as long as the growth crucible **110** continues to move downwardly into the lower zone **104**.

[0004] Returning to Figure 1A, the crystal pre-melt 108 is made by subjecting relatively pure crystal raw material in powder or granular form to a pre-melt step. The main purpose of the pre-melt step is to increase the bulk density of the crystal raw material so that the volume of the crystal growth furnace can be used efficiently. For example, synthetic CaF_2 powder has an apparent density of 1.1 g/cm^3 , and crystals grown from CaF_2 powder have an apparent density that is close to the theoretical density of CaF_2 , i.e., 3.18 g/cm^3 . Thus, if synthetic CaF_2 powder is used directly as the crystal raw material, two-thirds of the volume of the crystal growth furnace will not be used, or at least, not used efficiently. Through a pre-melt step, the apparent density of the CaF_2 raw material can be increased to approximately 2.2 g/cm^3 , which would be much closer to the density of the grown CaF_2 crystal.

[0005] The pre-melt step typically includes a treatment step in which oxide impurities are scavenged from the crystal raw material prior to melting the crystal raw material. Commonly, the treatment step involves mixing a solid fluorinating agent, e.g., PbF_2 , ZnF_2 , or polytetrafluoroethylene (PTFE), with the crystal raw material and then heating the mixture to the melting point of the crystal raw material. At this temperature, the solid fluorinating agent reacts with oxides in the crystal raw material to form volatile gases that escape from the crystal raw material. However, use of solid fluorinating agent to scavenge oxide impurities has a drawback in that impurities such as Pb^{2+} , Zn^{2+} , or C can remain in the crystal raw material after treatment. For optical fluoride crystals, the presence of these impurities, even at trace levels, can result in absorption bands that are detrimental to transmission at wavelengths below 200 nm.

[0006] Recently, gaseous fluorinating agents, such as CF_4 , HF, SF_6 , and BF_3 , have been proposed as alternatives to solid fluorinating agents in scavenging oxide impurities. With gaseous fluorinating agents, the risk of leaving harmful impurities such as Pb^{2+} , Zn^{2+} , or C in the grown crystal is relatively low or non-existent. However, use of gaseous fluorinating agents in scavenging oxide impurities in conventional settings poses various challenges. For example, the furnace and furnace elements, e.g., crucibles, thermocouples, and resistors, used in the pre-melt step are typically made of pure graphite or other materials that are susceptible to corrosion by the gaseous fluorinating agents, especially in the presence of oxygen atmosphere and/or at elevated temperatures. For example, CF_4 attacks thermocouples at temperatures above 1100°C . Further, pure graphite is porous and tends to outgas. Outgassing

of H₂O, CO₂, or CO from the graphite parts may contribute to contamination of the crystal pre-melt after treatment.

[0007] From the foregoing, there is desired a practical method of making a crystal pre-melt from crystal raw material involving use of a gaseous fluorinating agent as an oxide scavenger.

Summary of Invention

[0008] In one aspect, the invention relates to an apparatus for making a crystal pre-melt. The apparatus comprises a hermetically-sealable muffle furnace made of a non-porous refractory material, at least one port for entry and exit of gaseous substance within the muffle furnace, a temperature-controlled zone defined inside the muffle furnace, and a crucible for holding crystal raw material in solid or molten form inside the muffle furnace.

[0009] In another aspect, the invention relates to a method of making a crystal pre-melt. The method comprises disposing crystal raw material in loose powder, pressed powder, granular, or densified form in a temperature-controlled zone defined in a muffle furnace made of a non-porous refractory material and hermetically sealing the muffle furnace. The method further includes heating the temperature-controlled zone to a treatment temperature that enables reaction between a fluorinating agent and oxides in the crystal raw material, reacting the fluorinating agent with the crystal raw material to produce volatile gases, removing the volatile gases from the muffle furnace, heating the crystal raw material to form a melt, and solidifying the melt to form the crystal pre-melt.

[0010] Other features and advantages of the invention will be apparent from the following description and the appended claims.

Brief Description of Drawings

[0011] Figures 1A and 1B illustrate a Bridgman-Stockbarger process for growing crystals.

[0012] Figure 2A is a schematic of an apparatus for forming a crystal pre-melt according to one embodiment of the invention.

[0013] Figure 2B shows crystal raw material in a molten condition in a crucible disposed in a muffle furnace according to one embodiment of the invention.

[0014] Figure 2C shows the molten material in Figure 2B solidified into a crystal pre-melt according to one embodiment of the invention.

[0015] Figure 2D shows the molten material in Figure 2B being shaped into pellets according to another embodiment of the invention.

[0016] Figure 2E shows a crystal raw material preform suspended above a crucible inside a muffle furnace according to another embodiment of the invention.

Detailed Description of Preferred Embodiments

[0017] The invention will now be described in detail with reference to a few preferred embodiments, as illustrated in accompanying drawings. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the invention. However, it will be apparent to one skilled in the art that the invention may be practiced without some or all of these specific details. In other instances, well-known features and/or process steps have not been described in detail in order to not unnecessarily obscure the invention. The features and advantages of the invention may be better understood with reference to the drawings and discussions that follow.

[0018] Embodiments of the invention provide an apparatus and a method for making a crystal pre-melt from crystal raw material. The method involves use of a fluorinating agent to scavenge oxide impurities from the crystal raw material prior to forming the crystal pre-melt. The apparatus includes a muffle furnace made of a non-porous refractory material, such as quartz, alumina, silicon carbide, vitreous carbon, vitreous graphite, or glassy carbon-coated graphite. By constructing the muffle furnace from a non-porous refractory material, the crystal raw material is protected from contamination through outgassing of the muffle furnace material. Also, the non-porous refractory material is inert in the sense that it does not react with the process gases under the process conditions used in making the crystal pre-melt.

[0019] The crystal pre-melt made by the apparatus and method of the invention could be used to grow crystals. The type of crystals grown would depend on the composition of the crystal raw material from which the crystal pre-melt is made. One group of crystal raw

material that is of interest herein is fluoride crystal raw material. In one embodiment, the fluoride crystal raw material includes a metal fluoride selected from the group consisting of CaF_2 , BaF_2 , MgF_2 , SrF_2 , LiF , NaF , $(\text{M}_1)_x(\text{M}_2)_{1-x}\text{F}_2$, and M_3AlF_6 , and mixtures thereof, where M_1 is selected from the group consisting of Li and K; M_2 is selected from the group consisting of Ca, Ba, Mg, and Sr; M_3 is selected from the group consisting of Li, Na, K, Rb, and Cs; and x is in the range from 0 to 1, preferably in a range from 0.01 to 0.99. The fluoride crystal raw material may also include mixed metal fluorides wherein a metal fluoride selected from the lanthanide series, for example, lanthanum, ytterbium, yttrium, or others of the series, is used as one of M_1 or M_2 , or is used in addition to M_1 and M_2 . Those skilled in the art will recognize the possible combinations.

[0020] Referring now to Figure 2A, an apparatus 200 for making a crystal pre-melt according to an embodiment of the invention includes a muffle furnace 202 that is constructed from a non-porous refractory material. Examples of suitable non-porous refractory materials include quartz, alumina, silicon carbide, vitreous carbon, vitreous graphite, glassy carbon-coated graphite, and a combination of these materials. These materials are also inert in that they are not expected to react with the process gases under the process conditions in which the crystal pre-melt will be made inside the muffle furnace 202. By constructing the muffle furnace 202 from a non-porous refractory material, the crystal pre-melt made inside the muffle furnace is protected from contamination through outgassing of the muffle furnace material.

[0021] The upper and lower ends 203, 205 of the muffle furnace 202 are covered with end caps 204, 206, respectively. Preferably, the end caps 204, 206 make a sealed contact with the muffle furnace 202, providing a hermetically-sealed environment inside the muffle furnace 202. A variety of sealing mechanisms, such as metal-to-metal seal, O-ring seal, etc., can be used between the muffle furnace 202 and the end caps 204, 206 to achieve the sealed contact. To avoid contamination of the crystal pre-melt through outgassing of the end cap material, the end caps 204, 206 are also preferably constructed from a non-porous refractory material, such as listed above for the muffle furnace 202.

[0022] Either or both of the end caps 204, 206 or the wall of the muffle furnace 202 may include one or more ports through which gases can flow into and out of the muffle furnace 202. As illustrated in Figure 2A, an inlet port 212 is provided in the end cap 204. The inlet port 212 may be selectively connected to gas sources 214, 216. As an example, the gas

source **214** could contain a gaseous fluorinating agent, and the gas source **216** could contain an inert gas. Valves **215** may be provided to control rate of flow from the gas sources **214**, **216** into the muffle furnace **202**. In Figure 2A, an outlet port **218** is also provided in the end cap **204**. The outlet port **218** may be connected to an effluent treatment chamber **220**, which may include a scrubber (not shown) to remove or decompose any gaseous fluorinating agent in the effluent of the muffle furnace **202**. Examples of scrubbers include heated metal oxide such as soda lime or a plasma system. Although not shown, a vacuum system could also be incorporated to suck out gas from the muffle furnace **202** through the outlet port **218**.

[0023] In one embodiment, a variable temperature heater **222**, which may be made of one or more heating elements, is mounted outside the muffle furnace **202** to maintain a desired temperature in at least a zone **223** of the muffle furnace **202**. When more than one heating element is used the elements can be individually controlled to provide greater temperature flexibility. The temperature in the zone **223** of the muffle furnace **202** can be measured using thermocouples **224**, and the output of the thermocouples **224** can be used to control the power supplied to the heater **222**. To avoid contact between the thermocouples **224** and process gases in the muffle furnace **202**, the thermocouples **224** are preferably mounted external to the muffle furnace **202**, e.g., on the outside wall **225** of the muffle furnace **202**. To allow uniform heat distribution inside the zone **223** during operation, the heater **222** may be moved, e.g., rotated or translated, relative to the zone **223**.

[0024] The invention is not limited to use of an external heat source, such as variable temperature heater **222**, to provide a desired temperature profile in the zone **223**. Inductive heating or resistive heating could also be used to provide the desired temperature profile in the zone **223**. For example, in a situation where the muffle furnace **202** is made of a conductive non-porous refractory material, such as vitreous graphite, vitreous carbon, or silicon carbide, the muffle furnace **202** could be used as an electromagnetic induction susceptor when coupled with an induction coil. Alternatively, the muffle furnace **202** itself could serve as a heating element if a controlled current is placed across it.

[0025] In one embodiment, a crucible **208** is supported in the temperature-controlled zone **223** of the muffle furnace **202**. As an example, the crucible **208** could be suspended in the zone **223** on a handle **210** that is coupled to the end cap **204**. In Figure 2A, the crucible **208** holds the crystal raw material **226** to be transformed into a crystal pre-melt. The handle **210** could be coupled to the end cap **204** in such a way that it allows the crucible **208** to be

movable inside the zone 223. For example, it may be advantageous to rotate and/or translate the crucible 208 inside the zone 223 so that the crystal raw material 226 is uniformly exposed to the process gases and/or uniformly heated. To prevent contamination of the crystal raw material 226, the crucible 208 and handle 210 are preferably constructed of an inert refractory material. To avoid contamination of the crystal raw material 226 through outgassing of crucible/handle material, the inert refractory material is preferably non-porous.

[0026] The invention is not limited to suspension of the crucible 208 in the muffle furnace 202 through use of the handle 210. For example, the crucible 208 could be supported on a platform (not shown), which is itself supported inside the muffle furnace 202. A mechanism (not shown) may be coupled to the platform to rotate and/or translate the platform inside the muffle furnace 202 if desired.

[0027] In one embodiment, a method of making crystal pre-melt involves loading crystal raw material 226 in powder or granular form into the crucible 208. The crystal raw material 226 may initially have a high oxygen content, e.g., much greater than 200 ppm by weight. The crucible 208 is then suspended or supported inside the temperature-controlled zone 223 of the muffle furnace 202, and the end caps 204, 206 are fitted at the ends of the muffle furnace 202 to provide a gas-tight environment inside the muffle furnace 202. Next, the muffle furnace 202 is purged and filled with a purge gas, which is typically an inert gas such as argon, helium, or nitrogen. Alternatively, the muffle furnace 202 can be first evacuated, e.g., through the use of a vacuum system, and then filled with a purge gas.

[0028] The sealed muffle furnace 202 is heated, typically from room temperature, to treatment temperature. Heating may occur simultaneously with purging and/or filling the muffle furnace 202 with a purge gas. Heating to purification temperature can occur in one step or in multiple steps and may include one or more stabilization steps. The treatment temperature may be below, at, or above the melting point of the crystal raw material 226. In general, the treatment temperature should be high enough to enable reaction between the crystal raw material 226 and the fluorinating agent to be used in scavenging oxide impurities from the crystal raw material 226. To facilitate diffusion of gases through the crystal raw material 226, the treatment temperature should not be so high as to significantly increase the density of the crystal raw material 226 during the treatment phase.

[0029] When the treatment temperature is reached, the inert gas in the muffle furnace **202** is replaced with a gaseous fluorinating agent, such as CF_4 , NF_3 , SF_6 , BF_3 , C_2F_4 , HF , F_2 , or a mixture of these fluorides, or similar fluorination gases, for example gaseous XeF_2 , known in the art. The gaseous fluorinating agent may be carried into the muffle furnace **202** in a stream of inert gas, such as argon, helium, or nitrogen. The amount of gaseous fluoride in the inert gas stream may be in a range from 1% to 100% by weight. The inert gas may be premixed with the gaseous fluorinating agent or provided from a separate source. In one embodiment, the flow rate of the gaseous fluorinating agent is adjusted such that the pressure in the muffle furnace **202** is in a range from 0.1 to 5 atm., preferably around 1 atm. The gaseous fluorinating agent is selected based on its decomposition temperature and the melting point of the crystal raw material **226**. For example, CF_4 has a high bond energy (536 KJ/mol) and is expected to be an effective oxide scavenger at temperatures of 1000°C. Thus, CF_4 is better suited for treatment of high-melting crystal raw materials such as CaF_2 . NF_3 and SF_6 are expected to produce similar scavenging effect as CF_4 at temperatures closer to 200 to 400°C and 500 to 800°C, respectively, and are thus better suited for the treatment of low-melting crystal raw materials.

[0030] The crystal raw material **226** is exposed to the gaseous fluorinating agent for a selected time period; for example, 1-240 hours, preferably 10-100 hours. During this period, the gaseous fluorinating agent reacts with oxide impurities in the crystal raw material **226** to produce volatile gases, which are carried away to the effluent treatment chamber **220**. The amount of oxide impurities removed from the crystal raw material **226** depends on the exposure time and treatment temperature. In general, the time required to remove oxide impurities decreases as treatment temperature increases. Also, the closer the treatment temperature is to the melting point of the crystal raw material, the shorter the time required to reduce the oxide impurity level of the crystal raw material. Gas analysis of the effluent from the muffle furnace **202** can be used to determine the completion of the treatment step. For example, the oxygen concentration of the muffle furnace effluent may be measured, and when this oxygen concentration falls below a predetermined threshold, the treatment process can be stopped.

[0031] When the treatment process is completed, the muffle furnace **202** is purged with a purge gas, which typically is an inert gas such as helium or argon. The muffle furnace **202** is then heated to a temperature sufficient to melt the crystal raw material **226**. Figure 2B shows

the molten crystal raw material **226a** inside the crucible **208**. The molten crystal raw material **226a** is then solidified by rapid cooling to form a crystal pre-melt. Figure 2C shows the crystal pre-melt **228** inside the crucible **208**. The solidification step does not include crystal growth in the sense that the molten material is not moved through a thermal gradient. At this point, the crystal pre-melt **228** may be removed from the muffle furnace **202** and stored in a dry inert atmosphere, e.g., in a sealed container purged by an inert gas or a container sealed under vacuum, to prevent contamination before the crystal growth step. Generally speaking, to reduce melting time in the growth furnace, the crystal pre-melt **228** will have to be crushed before it is loaded into the growth furnace. This crushing action can be a source of metallic and other forms of contamination in the crystal pre-melt **228**. To avoid the crushing step, the crystal pre-melt **228** could be divided into smaller shapes inside the muffle furnace **202**.

[0032] As illustrated in Figure 2D, the molten crystal raw material **226a** can be formed into pellets **230**, as taught by Alexandre M. Mayolet in U.S. Patent No. 6,451,106 (assigned to Corning Incorporated), to avoid the crushing step. In Figure 2D, the crucible **232** used in holding the molten crystal raw material **226a** has an opening **234** in its base. The opening **234** permits the molten material **226a** to drop from the crucible **232** into a receptacle **242** positioned below the crucible **232**. A removable cover **236** (shown in phantom) at the opening **234** prevents the molten material **226a** from passing through the opening **234** until the operator so elects. The mechanism for removing the cover **236** is not illustrated, but may, for example, include a slide rod terminating outside the muffle furnace **202**. A baffle or diaphragm **238** may be placed at a location below the level of the heater **222** to create a temperature differential between the melting zone **223** (defined by the heater **222**) and a dropping zone **240** below the heater **222** where the drops of molten material **226a** will solidify. The size of the droplets will be dictated by the diameter of the opening **234** at the bottom of the crucible **232**.

[0033] In another embodiment of the invention, the crystal raw material used in making the crystal pre-melt is provided as a porous preform. The porous preform could be made by isostatic pressing of crystal raw material, as taught by Malcolm Ivy in U.S. Patent Application Serial No. 10/611,506 (assigned to Corning Incorporated). Briefly, the process for forming the porous preform includes loading crystal raw material in powder form into a flexible mold and then applying isostatic pressure to the mold to compress the crystal raw material. The isostatic pressing could be cold, warm or hot. To facilitate handling of the

preform, a preform handle made of crystal or a non-porous refractory material, such as previously listed for the muffle furnace material, could be inserted in the top of the crystal raw material so that it is molded to the top of the crystal raw material during the isostatic pressing. Alternatively, a notch can be cut at the top of the preform after isostatic pressing, and a preform handle can be inserted in the notch to facilitate handling of the preform.

[0034] Figure 2E shows a porous preform **250**, made of crystal raw material, suspended in the muffle furnace **202**. As an example, the porous preform **250** could be suspended using a preform handle **254** having one end inserted into the porous preform **250** and the other end coupled to the end cap **204**. Alternatively, the porous preform **250** can be suspended by, for example, a claw-like device grasping the outside of the preform. The claw-like device is such that it exerts continuous pressure on the preform so that the preform is held in position above the waiting crucible **208** during the treatment and melting steps. The porous preform **250** is treated in the muffle furnace **202** in the same manner previously described for the powdered or granular crystal raw material. The advantage in this case is that there is no crucible in the flow path of the gaseous fluorinating agent and the porous preform **250**. Thus, quicker diffusion of the gaseous fluorinating agent through the porous preform **250** is enabled, and contamination of the preform **250** with crucible material is avoided. After treating the preform **250**, the preform **250** can be melted into the waiting crucible **208**. A lift mechanism **252** having a sliding member **256**, such as a piston or rod, could be coupled to the crucible **208** to move the crucible into the zone **223** where the preform **250** is melted. As an example, the lift mechanism **252** could be a fluid-powered actuator, such as a hydraulic or pneumatic actuator, or a mechanical actuator. The melted preform **250** can be cooled into a crystal pre-melt as previously described. Alternatively, the melted preform **250** could be shaped into pellets, as described above, or into other appropriate shapes that would allow the crushing step to be bypassed.

[0035] In one example, CaF_2 crystal pre-melt is made using the apparatus and method described above. The process outline is as follows:

- Load CaF_2 raw material, if in powder form, into a crucible.
- Suspend the crucible containing the CaF_2 raw material or suspend the CaF_2 preform in a cold muffle furnace and seal the muffle furnace.

- Purge the muffle furnace and fill the muffle furnace with an inert gas, such as argon or helium, at atmospheric pressure + 1 psig (0.068 atm) as the muffle furnace is heated to 800°C.
- Optionally allow the muffle furnace to stabilize at 800°C in the inert gas for several hours.
- Ramp up the temperature in the muffle furnace to 1000°C with the same gas and pressure.
- At 1000°C, replace the inert gas in the muffle furnace with CF₄ to purify the CaF₂ raw material. To reduce the amount of CF₄ used, the CF₄ may be cycled in and out of the furnace, rather than maintaining a constant flow through the system. Alternatively, a mixture of CF₄ and an inert gas may be used.
- Once the CaF₂ has been purified, replace CF₄ with inert gas, preferably argon.
- Once only the inert gas is in the muffle furnace, heat the muffle furnace to above 1440°C, preferably 1480°C, so that the CaF₂ may melt into a pure liquid.
- Cool the melted CaF₂ liquid using a variety of temperature rates (that is, programmed cooling) to form a solid body, i.e., the crystal pre-melt.

[0036] Other single metal fluorides or mixed metal fluorides can be prepared in a manner similar to the one described above. Further, although it is preferable to scavenge oxide impurities using gaseous fluorinating agents, the crystal raw material, in loose powder or granular or pressed form, may optionally include a small amount of a solid fluorinating agent, e.g., 0.5 to 2 wt% of PbF₂, ZnF₂, or other solid fluorinating agent known in the art, for scavenging oxide impurities. In this case, at the treatment temperature, the solid fluorinating agent would react with the oxide impurities in the crystal raw material, and there may be no need to introduce a gaseous fluorinating agent into the muffle furnace to scavenge the oxide impurities from the crystal raw material. However, if desired, the gaseous fluorinating agent can be used in conjunction with the solid fluorinating agent to scavenge oxide impurities from the crystal raw material.

[0037] The invention provides one or more advantages. Using a muffle furnace made from non-porous refractory material protects the crystal raw material from contamination due

to outgassing of the muffle furnace material. Thermocouples can be mounted on the outside of the muffle furnace wall to prevent them from being attacked by the process gases. The level of process control over temperature, pressure, and process gas is better in a sealed muffle furnace environment than in a sealed furnace constructed from pure graphite. The option to divide the crystal pre-melt into pellets or other similar shapes would eliminate the need to crush the crystal pre-melt for the crystal growth step.

[0038] While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.